

Liquid hydrocarbons obtained by thermal conversion of biomass/plastic mixtures

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Introduction

The utilization of plant biomass residues and waste plastics to valuable products by thermal co-treatment processes is the important direction of recent research activity. Polyolefines contain rather high amount of hydrogen and they provide hydrogen at thermal co-processing with coal increasing the yield of light hydrocarbon fraction [1]. The mixture of wood biomass with polyethylene was successfully converted to liquid products [2-3].

The main task of this work was to establish the influence of co-treatment process conditions on the yield and composition of liquid products from biomass/plastic mixtures.

Experimental

Liquefaction experiments were carried out in 0,25 l rotating autoclave. A mixture of dry plant biomass (pine-wood, beech-wood, lignin, cellulose), plastic (polyethylene, isotactic-polypropylene, atactic polypropylene) and in some cases catalyst (5% wt.) was loaded into autoclave, pressurised with argon up to 0.1 MPa or hydrogen up to 3.0 – 5.0 MPa and then heated up 340-480°C during 1 h. After cooling the autoclave, gas products were collected and analysed by gas chromatography technique. Light liquid products (b. p. < 180°C) and water fraction were distilled *in vacuo*. The other products were extracted with benzene.

GC - MS analyses of light liquid products was carried out using 40 m ? 0,3 mm silica phased capillary column coated with SE-30 and connected with VG-70HS mass spectrometer. Heavy liquid products (b.p. > 180°C) were analyzed by ¹³C n.m.r. spectroscopy ("Bruker" MSL-400). For characterization of the heavy liquid products, they were separated on a particular families of compounds by a column chromatography method with registration of fluorescence emission spectra. Educued fractions were analyzed by g.c. - m.s. technique.

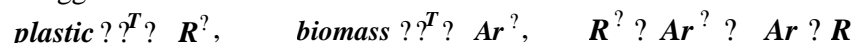
Results and discussion

Biomass/plastic pyrolysis

The degree of biomass/plastic mixture conversion (72-80%) did not significantly change with co-pyrolysis temperature variation within the range 370-460°C. The main effect of high temperature is the increased amount of gaseous products with synchronous decreasing of liquids yield. The maximum yield of liquids (about 50% wt.) was obtained at 370-400°C. In all runs the degree of conversion was increased with the growth of plastic concentration in biomass/plastic mixture. The variation of biomass nature has much less effect.

The yields of light liquids (b.p. < 180°C) of mixture pyrolysis are by 2-2,5 times higher as compared with expected ones, calculated as a sum of light liquids produced from the each separate component of biomass/plastic mixture. The highest yield of light hydrocarbon fraction (25.0% wt.) was obtained with cellulose and the less one (17.1% wt.) with hydrolytic lignin. Gaseous products of biomass/plastic co-pyrolysis contain by 10 times less of olefins then that of plastic (PE, PP) pyrolysis. This fact can indicate that unsaturated plastic-derived products react with products of biomass thermal depolymerization with liquids formation. Taking into account the known ideas about mechanism of synthetic and natural polymers thermal decomposition the scheme of biomass/plastic mixture

co-pyrolysis was suggested:



This scheme explains the observed synergistic effects by interaction of aliphatic radicals formed during plastic cracking with radicals of aromatic nature derived from plant biomass.

Biomass/plastic hydrolypyrolysis

The hydrolypyrolysis of biomass/plastic mixture results in higher degree of conversion (by 1.2 times) and in increased yield of light liquids with b.p. < 180°C (by 1.6-1.8 times) as compared to co-pyrolysis in an inert atmosphere.

The addition of activated iron ore catalysts also increases the degree of mixture conversion and the yield of light hydrocarbon fraction. Pyrrhotite catalyst yields the highest amount of the light fraction (40% wt. for beech-wood/PE mixture with ratio 1:1 at 400°C). The highest degree of conversion (91% wt.) was observed for activated haematite catalyst. The formation of light liquids is promoted by H₂ pressure, which suppresses the char formation and facilitates the thermal cracking of heavy liquid products. The degree of pine-wood conversion was increased with the growth the plastic content in the mixture, but no effect was observed in the case of cellulose.

Products composition

The composition of heavy liquids of co-pyrolysis process significantly depends on biomass/plastic ratio. Wood pyrolysis liquids mainly contain polars (eluted with n-hexane) and polyaromatics (eluted with dichloromethane TGF mixture). The addition of plastic to wood biomass increases the concentration of saturates and light aromatics with synchronous decreasing by a few times the content of polar compounds.

The nature biomass has less influence on the composition of heavy liquids of biomass/plastic co-pyrolysis process. Eluted with hexane fraction from heavy liquids of lignin/PE (1:1) and pine-wood/PE co-pyrolysis have the similar composition according to GC-MS data. The more significant influence of plastic nature on the composition of fractions eluted by hexane was detected. The liquid of beech-wood/a-PP co-pyrolysis contains a branched hydrocarbons which are absent in the liquid fraction of beech-wood/PE co-pyrolysis. Both fractions have a large amount of docosane (C₂₂H₄₆). According GC-MS data the light liquids of biomass/plastic hydrolypyrolysis contain mainly normal paraffines C₇-C₁₃ (about 75% for pine-wood/i-PP mixture), alkylbenzenes and alkylfuranes compounds (about 10%) and non-identified compounds (about 15%).

The liquids of biomass/plastic pyrolysis and hydrolypyrolysis can be used as chemical feedstock and their light hydrocarbon fraction as motor fuel component.

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